

Bengt Nelander

Molecular Potential Energy Surfaces
some Experimental and Theoretical Aspects

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This review gives a summary and discussion of the results from the following papers which will be referred to by the Roman numerals I-X.

- I. Nelander, B. UV-Absorption Spectra of Complexes Between Some Disulfides and Iodine I. Acta Chem. Scand. 23 (1969) 2127.
- II. Nelander, B. UV-Absorption Spectra of Complexes Between Some Disulfides and Iodine II. Acta Chem. Scand. 23 (1969) 2136.
- III. Nelander, B. On the Structure of Organic Disulfides, Acting as Electron Donors. Spectrochim. Acta (Accepted for publication).
- IV. Nelander, B. and Sunner, S. Cogwheel Effect in Dialkyl Disulfides. J. Am. Chem. Soc. 94 (1972) 3576.
- V. Nelander, B. Simple Form for the Virial Theorem for Polyatomic Molecules. J. Chem. Phys. 51 (1969) 469.
- VI. Nelander, B. and Del Re, G. Chemical Bond and *Ab Initio* Molecular Calculations. J. Chem. Phys. 52 (1970) 5225.
- VII. Nelander, B. On the Quantum Mechanical Basis for Bond Energy Schemes. J. Chem. Phys. 55 (1971) 2949.
- VIII. Nelander, B. A CNDO/2 Calculation on a Complex between Ethylene and Chlorine. Theoret. chim. Acta (Berl.) 25 (1972) 382.
- IX. Fredin, L. and Nelander, B. On the Structure of the Ethylene Chlorine Complex. J. Mol. Structure (Accepted for publication).
- X. Fredin, L. and Nelander, B. An IR and CNDO Study of a Water Chlorine Complex. J. Mol. Structure (Accepted for publication).



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INTRODUCTION

Current theories of conformation analysis (1), molecular vibrations (2,3) and chemical kinetics (4) are based on the concept of the nuclear potential energy surface. That is, the assumption that to each nuclear configuration there corresponds a well defined potential energy, which together with the nuclear kinetic energy may be used to set up a Schrödinger equation for the nuclear motions (5).

Once the solutions of the nuclear Schrödinger equation are known, we may use statistical mechanics to calculate molecular properties at finite temperatures. Unfortunately our knowledge about potential energy surfaces is fairly limited (6).

In the following we will consider some experimental and theoretical methods which may be used to gain some insight into the nature of potential energy surfaces.

Purely Theoretical Methods

Theoretically, potential energy surfaces may be obtained from calculations of the total electronic energy for a number of nuclear configurations, together with numerical interpolation between the results. Such calculations have been performed for a number of diatomic molecules (7). In recent years successful calculations of barriers to rotation around single bonds (8) and to inversion (9) have been carried out. Ab initio calculations have also proved to be useful for solving problems in the interpretation of molecular vibration spectra (10). As a result it seems as if we soon will have available wave functions of almost Hartree Fock quality or better containing numerous simple structural elements, in different conformations.

Molecular wave functions are in general given as expansion coefficients for a specified basis set. It is by no means easy to identify the chemists' concepts of bonds and functional groups directly from the wave function. However, since they are such useful concepts in empirical chemistry, a large amount of work has been spent in analysing the results of ab initio calculations for representations of bonds. An early attempt to systematize the results of molecular calculations was Mulliken's population analysis (11). While of great practical value, its general applicability is severely limited by its complete basis set dependency. More recently different localisation schemes based on the early work by Lennard-Jones and coworkers have been utilized to find "bond orbitals" (12,13,14). However, these cal-

culations are handicapped by their dependency on the molecule from which the bond orbitals were obtained.

Paper VI represents an attempt to avoid the dependency of the bond representative (orbital, group function, density matrix term) on a particular molecule. A method is advocated where the bond representatives are found by an optimization procedure using a set of molecules containing a common bond. The optimized quantity is more or less arbitrary, for instance a sum of overlap integrals. This "measure of success" of the particular bond representative, was left arbitrary since there seems to be no best way to find bond representatives, considering the approximate nature of the concept of bonds or functional groups.

Paper VII represents, in part, a generalisation of Allen and Shull's paper (15) on the basis for bond energy schemes. The starting point is the observation that all one electron properties of a molecule (for instance dipole moment, forces on nuclei, electronic kinetic energy) may be obtained from the first order density matrix of the molecule (16).

$$\Gamma(11') = N \int dx_2 \dots dx_N \Psi(1,2,\dots,N) \Psi^*(1',2,\dots,N) \quad (1)$$

Besides, the exact wave function (within the Born Oppenheimer approximation) will fulfill the virial theorem:

$$T + W + \sum R_I \frac{\partial W}{\partial R_I} = 0 \quad (2)$$

T is the kinetic energy of the electrons, W is the total electronic energy (including nuclear repulsions) and the R_I 's are a set of distances which together with angular coordinates is sufficient to specify the nuclear configuration (see Paper V). Using the virial theorem, we may calculate the total energy from the first order density matrix. This means that if we are able to construct the first order density matrix of a molecule from a set of standard terms (for instance representing bonds), the total energy close to a nuclear equilibrium configuration, will be given by a sum of standard terms (slightly modified by the partial derivative terms in the virial theorem).

The total energy is directly obtained from the second order density matrix (16)

$$\Gamma_2(1,2|1',2') = \binom{N}{2} \int dx_3 \dots dx_N \Psi(1,2,\dots,N) \Psi^*(1',2',\dots,N) \quad (3)$$

$$W = \text{Tr}_1(\hat{h}_1 \Gamma_1) + \text{Tr}_{12}(\frac{1}{r_{12}} \Gamma_2) + V_{nn} \quad (4)$$

$$\hat{h}_1 = -\frac{1}{2} \nabla^2 - \sum_n \frac{Z_n}{r_{1n}} \quad (5)$$

$$V_{nn} = \sum_{m < n} \frac{Z_m Z_n}{R_{mn}} \quad (6)$$

Here Z_n is the charge on nucleus n , r_{1n} the distance between nucleus n and electron 1. R_{mn} is the distance between nuclei m and n and r_{12} the distance between electrons 1 and 2.

$$\Gamma_1(1|1') = \frac{2}{N-1} \text{Tr}_2 \Gamma_2(1,2|1',2') \quad (7)$$

Thus, if the results of calculations on small molecules could be analysed for standard terms, which may be used to construct the second order density matrix of a larger molecule, we would have a method for calculating its properties, without having to solve its Schrödinger equation. There is one problem which has to be solved in this case: $\Gamma(1,2|1',2')$ contains delocalized contributions which may loosely be described as electron 1 in one end of the molecule and electron 2 in the other. These contributions depend specifically on the molecule under consideration and a standardized way to deal with them has yet to be found. For the first order density matrix there is no similar problem.

Semiempirical methods

The methods outlined in the previous paragraph are at best very tedious. The potential energy surface has to be calculated point by point and numerical interpolation has to be used elsewhere (17). Consider for instance the difficulties which we would meet if we apply these methods to the conformation analysis of

cyclohexane derivatives. We realize that there is also a need for simpler ways to deal with molecular energy problems. One possibility is to approximate the potential energy surface close to equilibrium with a sum of energy contributions from bond stretching, bond bending, interaction between non bonded nuclei etc (18-21):

$$2W = \sum k_{ij}(r_{ij} - r_{ij}^0)^2 + \sum k_{ijk}(\theta_{ijk} - \theta_{ijk}^0)^2 + \sum V_{ij} \quad (8)$$

In this way one obtains an analytic expression for the energy surface, which makes it relatively easy to find nuclear equilibrium configurations, vibration frequencies etc. Potential energy functions of this sort have been used successfully, for instance to clarify the conformation analysis of medium sized cycloalkane rings. A serious problem in this type of approach is that there is no *a priori* way to specify the form of the potential energy terms. The only existing method for selecting the best form has been described as the survival of the fittest (22).

In this situation, some insight may be gained from simplified model force fields.

Parr and coworkers have developed quite successful electrostatic models (23-27) for bond stretching in diatomic molecules using the virial theorem and the Hellmann-Feynman theorems as starting points. These models have recently been generalized to three atomic molecules (28,29).

In connection with models of this kind it may be noted that the virial theorem is a partial differential equation for the total energy, from which the total energy may be obtained if we know the kinetic energy everywhere. The homogeneous equation we get by putting $T = 0$ is Euler's relation for a homogeneous function of degree -1 (30). This means that if we add a homogeneous function of degree -1 to any particular solution of the full partial differential equation, we get another solution. The desired solution must be fixed with a boundary condition on a hypersurface (29).

It has recently been argued by Tanaka and Parr (31) that the virial theorem, as given in paper V may serve as a basis for the electron pair repulsion model of Gillespie and Nyholm (32) and for Walsh's rules (33).

In his classic series of papers, on the shape and electronic structure of small molecules, Walsh showed that a set of curves depicting some orbital "binding energies" as functions of some angular parameter, were very useful in predicting the shape of small molecules. Both ground states and excited states were considered. Walsh did not specify his "binding energies" and considerable efforts have been spent on attempts to find their quantum mechanical counterparts (34).

If we assume, that we keep all bond lengths at the equilibrium values, corresponding to a given value of an angular parameter in some molecule, then the virial theorem becomes:

$$W = -T = \sum_i n_i t_i \quad (9)$$

Here the n_i and t_i are occupation numbers and kinetic energies of the natural orbitals (16).

In the Hartree Fock approximation, n_i is one or zero depending on if the orbital is occupied or not. If Walsh's binding energies are identified with the orbital kinetic energies, the required additive partitioning is obtained. Finding an additive partitioning represents only one part of the problem, one also has to find the changes of the orbitals with the angular parameter. Considering the general applicability of Walsh's rules, it seems as if one has to demonstrate that the orbital kinetic energies vary qualitatively as Walsh's binding energies, for a wide selection of situations.

Experimental methods, introduction

Experimentally, direct information about potential energy surfaces may be obtained from a careful analysis of vibration rotation spectra. Here the potential energy surface is represented by a Taylor expansion at a nuclear equilibrium configuration, and the expansion coefficients are determined independently of each other.

Because of the large number of independent constants needed to specify the potential energy surface, this method has been applied only to very small molecules (35-37). For larger molecules, all attempts to obtain a potential energy surface has to start from some model, which reduces the number of independent parameters, while still retaining the essential degrees of freedom (38).

In paper IV, a simple model for a part of the potential energy surface of organic disulfides is developed. The starting point is the observation from molecular models, that for certain positions of the alkyl group on one side of the disulfide bond, the other alkyl group cannot rotate freely, around its CS-bond. This observation is incorporated into the model in the simplest possible fashion, in order to elucidate its thermodynamic consequences. The alkyl groups are treated as made up of hard spheres and the rotation around the CS-bond is assumed to be free except for the steric interaction between the alkyl groups. The model is used to calculate values for the equilibrium constants of the disproportionation reaction:

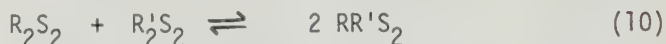


Table I gives a comparison between experimental equilibrium constants and the results of the model calculations. The good agreement may be taken as evidence that the central feature of the model, the coupled motions of the alkyl groups, has a real significance. It should be noted that although the model used in paper IV is very crude, the effect is real as is seen from the following more realistic argument. From the equation

$$GFL = L\Lambda \quad (11)$$

in external symmetry coordinates, we get (2):

$$\prod_{i=1}^{3N-6} \nu_i^2 = \frac{|F|}{4\pi^2 c^2} M^3 I_x I_y I_z \prod_{i=1}^{3N} \frac{1}{m_i} \quad (12)$$

Here the ν_i 's are the fundamental frequencies, m_i the masses of the atoms of the disulfide, M its total mass and I_x , I_y and I_z its principal moments of inertia, $|F|$ is the determinant of the force constant matrix. Now consider the three disulfides R_2S_2 , R'_2S_2 and $RR'S_2$. The higher frequencies of $RR'S_2$ are also fundamentals of R_2S_2 and R'_2S_2 . (Consider for instance the success of the group frequency concept (39).) The only frequencies, that may differ significantly are rather low frequencies, for the sake of argument we treat them classically. Their contributions to the partition function are factors of the form:

$$kT/h\nu_i \quad (13)$$

Using the expression for the translational and rotational partition functions

$$Q_{\text{trans}} = (2\pi M k T / h^2)^{3/2} \quad (14)$$

$$Q_{\text{rot}} = (8\pi^2 k T)^{3/2} (I_x I_y I_z)^{1/2} \sqrt{\pi} / \sigma h^3 \quad (15)$$

(Here σ is the symmetry number, $\sigma = 2$ for symmetric disulfides and $\sigma = 1$ for unsymmetric disulfides.)

We get

$$Q = \prod_i \left(\frac{kT}{h\nu_i} \right) (2\pi M k T)^{3/2} (8\pi^2 k T)^{3/2} (I_x I_y I_z)^{1/2} \frac{\sqrt{\pi}}{\sigma h^3} \quad (16)$$

The product is extended only over low frequencies. We introduce this expression into the equation for the equilibrium constant

$$K = \frac{Q^2(RR'S_2)}{Q(R_2S_2)Q(R'_2S_2)} \cdot e^{-\frac{\Delta E}{kT}} \quad (17)$$

and multiply numerator and denominator with the remaining fundamentals, which from the argument above are common to disulfides in the numerator and denominator. We may now use equation (15) to simplify the expression. The result is

$$K = 4 \times \frac{|F(R_2S_2)| |F(R'_2S_2)|}{|F(RR'S_2)|^2} \cdot e^{-\frac{\Delta E}{kT}} \quad (18)$$

If we disregard interactions across the disulfide bond, the quotient between the determinants has to be very close to one. Experimentally $\Delta E = 0$ and thus K should be close to 4, as is found when neither R , nor R' have tertiary carbon atoms next to the disulfide bond.

How does the disulfide internal rotation potential function depend on the number of electrons in the disulfide bond?

Papers I, II, and III start out from Bergson's model of the disulfide bond (40). This model starts out from the two doubly filled 3p lone pairs of the two sulfur atoms. They are combined to form two orbitals

$$3p_{\Pi A} = N_A(3p_1 + 3p_2) \quad (19)$$

and

$$3p_{\Pi B} = N_B(3p_1 - 3p_2) \quad (20)$$

The remaining occupied orbitals of the disulfide are assumed to be independent of the dihedral angle, CSS/SSC, of the disulfide. The first UV-absorption band of simple cyclic and noncyclic disulfides, is assigned to a transition from the upper of the two 3p Π orbitals to an orbital which is independent of the dihedral angle. The orbital energies of the 3p Π orbitals are obtained from a Hückel-type argument, in terms of a parameter. The two lower broken curves of figure 1 illustrate their dependency on the dihedral angle. The value of the parameter is determined from a comparison between measured UV-spectra of a five ring disulfide and a non cyclic disulfide and the calculated orbital energy of the upper orbital for ca. 30° and 90°.

Bergson treats the potential function for rotation around the SS-bond in the spirit of Walsh's rules, the varying part of the energy is considered to be made up of additive contributions from the two 3p Π orbitals. He then finds that if both orbitals are doubly occupied, the equilibrium dihedral angle is 90° (Δ CSS/SSC). If one of the electrons in the upper orbital is missing, the disulfide ion should be planar. (Dihedral angle 0° or 180°.) It was suggested by McGlynn et al. (41) that if the occupation of the upper orbital is decreased as for instance when the disulfide acts as electron donor in a charge transfer complex, the dihedral angle should change from 90°. Paper I represents an attempt to investigate this idea, by recording the charge transfer (CT) spectra of iodine complexes of a number noncyclic and cyclic disulfides. Table II gives the position of the first charge transfer band found in this work. These data are used to estimate dihedral angles of the complexed disulfides by means of a model based on Mulliken's (42) theory for charge transfer complexes, Bergson's model for the disulfide bond and Franklin's method (43) to calculate ionisation potentials. The use of a rather complex model to obtain quantitative results, may obscure the important fact that the charge transfer absorp-

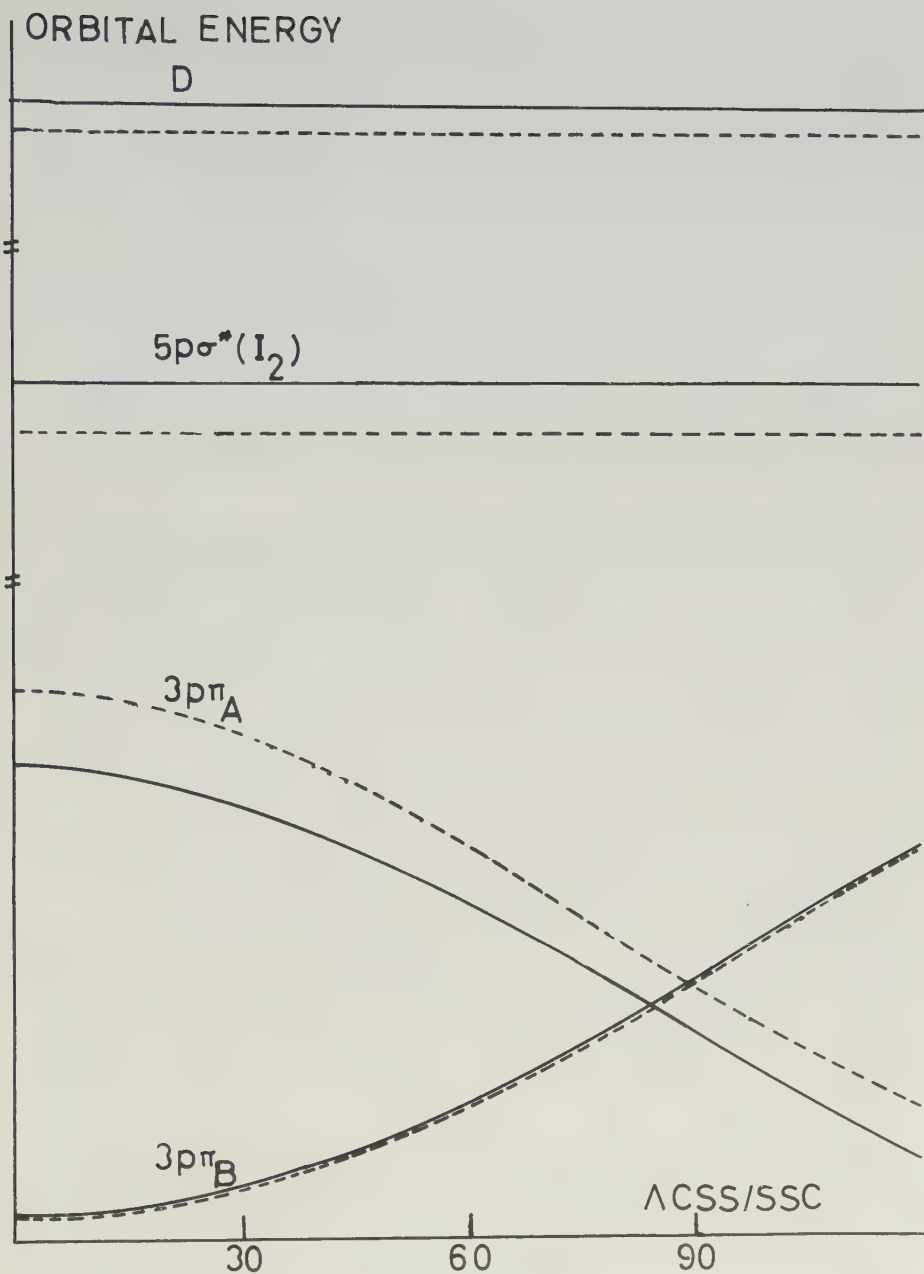


Figure 1

tion maxima do not vary in the expected way upon alkyl substitution. As expected they move to lower frequencies with increasing alkyl substitution on the β -carbon atom. In contrast, α -substitution moves the CT-maximum to higher frequencies. Not until three methyl groups have been introduced, does the CT-absorption start to move in the expected direction. In contrast, the CT-absorption of ordinary sulfides, behaves normally upon α -alkyl substitution (44).

As argued in paper III the quantitative estimates depend on the assumption of an axial model (see figure 2) for the disulfide complex. The other possible complex structure, the asymmetric structure (fig 2), treats the complexes as sulfide complexes, where one of the substituents is an S-alkyl substituent. From the point of view of this model, the behavior of the CT-absorption maximum, upon alkyl substitution should be completely unexpected.

If we accept the axial model, the estimated dihedral angles of the complexed disulfides, given in Table II, provide us with another estimate of the interaction between the alkyl groups on each side of the disulfide bond. It is seen from the table that the dihedral angle decreases significantly upon complex formation when the alkyl groups on both sides of the disulfide bond are methyl groups or at most have primary α -carbon atoms. In all other cases studied, the dihedral angle is more or less unchanged by complex formation. From observations on ball and stick models, this appears to be an unexpected result. For instance it seems surprising that the dihedral angle of $i\text{-Pr}_2\text{S}_2$ does not change approximately as that of Et_2S_2 . It should be possible for the $i\text{-Pr}$ groups to have their methyl groups rotated away from the line joining the two α -carbon atoms, and thus their interaction should be similar to that of the ethyl groups. However, the results of paper IV indicate that the two alkyl groups on each side of the disulfide bond like to rotate independently of each other. For $i\text{-Pr}_2\text{S}_2$, the conformation which permits a decrease in the dihedral angle does not allow the two $i\text{-Pr}$ groups to rotate, which means a considerable loss in entropy. It should therefore occur only at very low temperatures.

In this connection it must be noted that the energies required to bring about the changes in dihedral angle estimated from the model are quite modest. For instance, let us estimate the energy necessary to increase the dihedral angle from 90° to 100° , that is the "strain energy" of $t\text{-Bu}_2\text{S}_2$, implied by the estimate of the dihedral angle in Table II. We assume a potential function of the form

$$W = V_0^{1/2}(1 + \cos 2\theta) \quad (21)$$

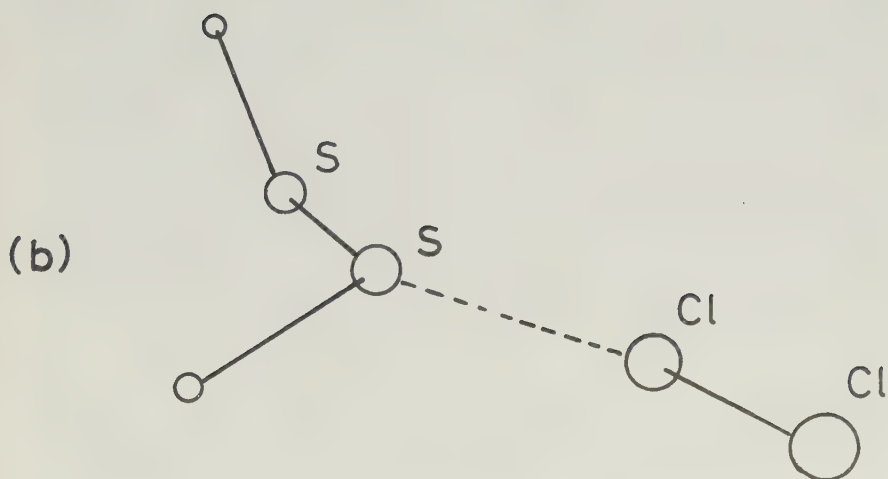
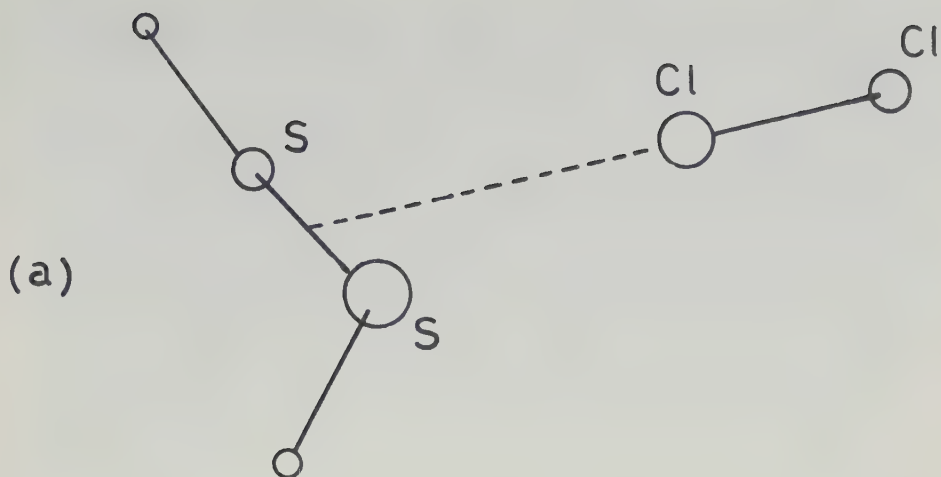


Figure 2

With $V_0 = 7$ kcal/mole (45,46) we get (θ is the dihedral angle $\Delta\text{CSS/SSC}$) ca. 0.1 kcal/mole, an excess energy, which cannot change the conclusions of paper IV.

Paper II reports a study of the disulfide iodine complexes at 77 K. It was undertaken in order to make sure that the complex spectrum dominated the recorded spectrum at all wave lengths. The original idea was to investigate the effect of complex formation upon the UV-absorption of the disulfides. It was found that this absorption was completely obscured by CT-absorption from the $3p\pi$ and $3p\pi^*$ orbitals of Bergson's model. The observed positions of the CT-maxima are given in Table III. It is seen from the table that the distance between the two maxima is larger the smaller the dihedral angle of the free disulfide.

Five membered ring disulfides ca. 30° (47) and 6-membered rings ca. 60° (48).

For the five membered rings the excitation energy difference is considerably smaller than might have been expected from Bergson's model. In paper II this apparent discrepancy is shown to be expected from Mulliken's resonance theory of CT-complexes. In a molecular orbital description of the complexes, it is noted that in the axial model, the upper of Bergson's orbitals, but not the lower, has the same symmetry as the anti bonding halogen orbital, to which the electron is excited by CT-absorption. These two orbitals therefore perturb each other, while the lower of Bergson's orbitals is essentially unaffected by the complex formation (see figure 1). When this perturbation is taken into account, the dihedral angles of the complexed disulfide may be estimated from the difference in CT-excitation energy. When the resulting dihedral angles are compared with those calculated from the position of the first CT-absorption maximum, a semiquantitative agreement is found (see Table III). In paper III, the investigation is extended to other acceptors than iodine. The spectra of the bromine, iodine chloride and sulfur dioxide complexes with disulfides, strongly resembles those of the iodine complexes. The model sketched above was used to estimate dihedral angles of the complexed disulfides also in these complexes. The results are included in Table III. The resulting dihedral angles are more or less independent of the acceptor. This might be interpreted as support for the suggestion from paper I, that the dihedral angle of the complexed disulfide is essentially determined by the interaction between its alkyl groups. Unfortunately the model used to calculate the dihedral

angles is too crude to allow quantitative comparisons between different acceptors. The remaining part of paper III is an attempt to justify some of the assumptions underlying the model used to calculate dihedral angles. To do this CNDO (49,50) calculations of UV-spectra of disulfides and disulfide chlorine complexes were carried out. Of course the CNDO approximation is too crude to allow any definite conclusions about the validity of the interpretation of the CT-spectra. However, it is based on assumptions independent of those underlying the model used above, and no experimental results on disulfides or charge transfer complexes have been used to determine its parameters. In spite of this it gives an almost quantitative description of the lowest UV-absorption of the cyclic and noncyclic disulfides studied here, if no d-orbitals on sulfur are included in the calculations. The CNDO calculations support the assumption of paper II, that the ionisation potentials of Bergson's orbitals vary approximately as the UV excitation energies of the free disulfides. However, the CNDO-calculations favor an asymmetric complex structure, for the disulfide chlorine complexes (chlorine was used since for this molecule the necessary CNDO parameters were available). The energy difference between the axial and asymmetric complex structures is small, and may perhaps be due to some artefact of the CNDO approximation. More important is that the UV-spectra which are calculated for asymmetric disulfide complexes are predicted to have two significantly different spectra corresponding to the two possible isomers of these complexes. This has not been observed, on the contrary, the CT-spectra of complexes of unsymmetric disulfides are entirely similar to those of symmetric disulfides.

The results of papers I to IV may be summarized as follows. Two methyl groups on each side of the disulfide bond do not interact significantly, the complex studies indicate that the carbon carbon distance may decrease by 0.2 Å, before a serious repulsion sets in. When the hydrogens of the two methyl groups are replaced by methyl groups, the rotations around the two CS-bonds ceases to be independent. The interaction between the two alkyl groups may be compared with that of two cog wheels, where the β -methyl groups act as cogs.

The investigations also support Bergson's model for the disulfide bond, both its orbital structure and its prediction that the dihedral angle of a disulfide is a function of the number of electrons in the bond.

IR-spectra and CNDO calculations as tools for investigations of potential energy surfaces

Papers VIII, IX and X represent an attempt to investigate the effect of the formation of weak complexes on the potential energy surfaces of the component molecules, by means of a combination of IR-studies and CNDO calculations. Paper VIII presents an exploratory CNDO calculation on an ethylene chlorine complex. It was undertaken to get an idea of the type of predictions, that may be expected from CNDO calculations. In keeping with considerations of orbital symmetry, the CNDO calculations predicted the existence of a stable complex, where the chlorine bond coincides with the C_2 axis of ethylene, orthogonal to the ethylene plane. The CNDO calculations also predicted that the chlorine stretching frequency should decrease significantly upon complex formation, that the complex should have an intense CT-absorption band, and that the UV-absorption of chlorine should be blue shifted by the complex formation. All these predictions were expected from comparisons with experimental results on other weak halogen complexes. Perhaps less expected is the prediction that the chlorine molecule becomes quite polarized in the complex. Indeed, the CNDO calculations suggested that the chlorine atom closest to the ethylene plane has a positive net charge. The internal charge transfer in the chlorine molecule is comparable to the charge transfer from ethylene to chlorine. There is another result of the CNDO calculations which is worth mentioning here. Most occupied orbitals of the two complex components are unperturbed by the complex formation. The only orbitals which do change significantly as a result of the complex formation are those of a_1 symmetry, when classified according to the point group of the axial complex, C_{2v} . That is, those which do not change under rotation around the C_2 axis or under reflection in the two symmetry planes of the complex. In fact the $2p\pi$ -orbital of ethylene mixes with the $3p\sigma$ -orbital of chlorine to form two orbitals with roughly equal contributions from both, and with a small but important contribution from the $3p\sigma^+$ of chlorine.

In paper IX, the CNDO calculations are extended to include the effect of complex formation on the ethylene molecule. As expected it is found that the C=C bond length increases slightly (0.007 Å) and that the hydrogens are bent out of the ethylene plane away from the chlorine (The calculated CC/CH₂ angle is 2.7^0).

Experimentally these predictions are hard to investigate. The main problems being to achieve a sufficiently high concentration of the complex and at the same time avoid reaction between the components.

The matrix isolation technique seems to be the best available method to solve these problems. In short the two components are mixed with inert gas and the two gas mixtures are allowed to condense together on a cold window. The complex forms during the condensation on the window. In this way it is possible to obtain a sufficiently large concentration of the complex to make it possible to study its IR-spectrum. Since all rotation of the complex as a whole, is completely hindered, all information which can be obtained about the complex structure is of an indirect nature. Important conclusions about the complex symmetry, may be drawn from the appearance in the complex spectrum of absorptions which are forbidden for the free components. In some cases more detailed information can be obtained through the product rule (2). For instance, if all fundamental frequencies of the same symmetry species as one of the rotations of the molecule as a whole, are known for two isotopic species of some molecule, the quotient between the two corresponding moments of inertia can be calculated. For weak complexes this means that the low frequency fundamentals, corresponding to the motions of the two components relative to each other, have to be determined, before the product rule can be used to investigate the over all structure of the complex. The product rules for the individual components of the complex will no longer be exact, but in favorable cases, they may be used to get some information about the component structure.

For the ethylene chlorine complex no absorption corresponding to fundamentals of A_u and B_{1g} symmetry in free ethylene were observed. (Paper IX.) This seems to imply a C_{2v} symmetric complex with the C_2 axis orthogonal to the ethylene plane, in agreement with predictions from the CNDO-calculations. Conclusions drawn from the absence of certain bands, are of course uncertain, for instance, neither the B_{2g} fundamental, nor all of the A_g fundamentals, were observed, in spite of that they are allowed for the C_{2v} symmetric complex predicted by the CNDO calculations. In this case the conclusions about the symmetry of the complex seem safe, since one of the unobserved bands is the torsion vibration of ethylene, which should have a major influence on the donor function of ethylene.

In the axial structure predicted by the CNDO calculations, the two chlorine atoms are nonequivalent, and therefore two different isomers of the ethylene $^{35}\text{Cl}^{37}\text{Cl}$ complex are possible. Considerable efforts were made to demonstrate this nonequivalence, by resolving the chlorine stretching absorption of the $^{35}\text{Cl}^{37}\text{Cl}$ complex into two components. However, both CNDO calculations and more elementary considerations caution against using

this failure as an argument against an axial structure. The chlorine-chlorine distance in the complex should vary strongly with the distance between the ethylene and chlorine molecules, and this coupling may very well eliminate the isomer shift of the chlorine stretching vibration.

Paper X gives an account of an experimental and CNDO study of the water chlorine complex. A series of CNDO calculations were carried out aiming at a determination of the complex structure. These calculations predicted a Y-shaped, planar complex, with insignificant changes in the water structure and a very small increase of the chlorine bond length. The calculations also predicted a significant decrease (ca. 2.5 %) of the water stretching frequencies and a small (ca. 0.6 %) decrease in the chlorine frequency. The water bending fundamental was predicted to be unaffected by complex formation. The measured IR-spectrum indicated that the chlorine interacted mainly with the oxygen of water. In agreement with the CNDO calculations, it was found that the bending frequency changes by only 0.02 %. But the changes in the stretching fundamentals were much smaller than expected from the CNDO calculations, 0.1 to 0.2 %. The isotope shift of the asymmetric stretching frequency of water was used to calculate the bond angles of the free water monomer and of the complexed water. In both cases the HOH angle was found to be close to 104° , in agreement with the CNDO result.

If the complex has the Y-shaped structure indicated by the CNDO calculations, the highest orbital of water which has the same symmetry as the $3p\sigma$ orbital of chlorine is the orbital marked " a_1 (lone pair)" in Walsh's original diagram for AH_2 molecules (33). In this diagram the "binding energy" of this orbital decreases very rapidly with increasing bond angle. We are thus lead to believe that electron donation from this orbital of water, will lead to an increase in the water bond angle. Experimentally no such change is found. This might be taken as evidence that water donates electrons essentially from its b_1 orbital (the $2p\pi$ orbital), which in Walsh's diagram is unaffected by a change in the bond angle. Thus we might expect a more or less pyramidal arrangement around the oxygen atom, similar to what Hassel and coworkers (51) have found for dioxane halogen complexes. However, since the CNDO calculations also predict an unchanged water bond angle for a Y-shaped complex, there seems to be no real basis for such a conclusion.

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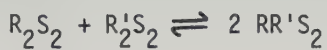
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Table I. A comparison between experimental and calculated equilibrium constants for the reaction



R	R'	K _{exp}	K _{calc}
Me	Et	5.6	4.5
Me	iPr	6.0	6.9
Me	t-Bu	42.5	49.0
Et	Pr	4.5	4.0
Et	iPr	4.5	4.8
Et	tBu	25.	26.3
iPr	tBu	15.	12.5

Table II. The position of the first CT absorption maximum of disulfide iodine complexes at room temperature and the estimated dihedral angle of the complexed disulfide.

Disulfide	CT-max (kK)	$\Delta(\text{CSS/SSC})$
Me_2S_2	32.06	21
Me EtS_2	32.17	15
Et_2S_2	32.30	11
Pr_2S_2	31.95	12
iBu_2S_2	31.57	14
Me tBuS_2	32.37	3.5
$\text{i-Pr}_2\text{S}_2$	31.94	3
$\text{s-Bu}_2\text{S}_2$	31.77	3
Et tBuS_2	32.00	2.5
i-Pr t-BuS_2	31.87	-
t-BuS_2	29.73	4.5 ^a
$\text{t-Am}_2\text{S}_2$	29.37	6 ^a
1,2 dithiane	28.64	12.5
1,2 dithiolane	26.86	-

$\Delta(\text{CSS/SSC})$, the decrease in the dihedral angle upon complex formation.

^aIncrease, see text.

Table III. Charge transfer absorption maxima and estimated dihedral angles for a series of disulfide complexes.

Donor	I ₂			Br ₂			S ₂ O ₂		
	ν_a	ν_b	θ_a	θ_b	ν_a	ν_b	θ_a	θ_b	
Me ₂ S ₂	30.8	34.6	61	70	31.4	36.0	48	64	
Et ₂ S ₂	32.2	34.9	79	73	31.0	34.6	53	66	
i-Pr ₂ S ₂	32.5	35.4	89	76	n	n			
i-Pr t-BuS ₂	32.3	35.1	91	76	n	n			
t-Bu ₂ S ₂	30.4	36.6	111	95	n	n			
1,2 dithiane	29.0	37.4	57	53	29.6	36.2	37	55	
2,3 dithia[4,5]spirodecane	26.3	39.9	<u>27.5^f</u>		29.1	41.2	<u>27.5^f</u>		
					27.3	44.1	<u>27.5^f</u>		

ν_a and ν_b charge transfer absorption maxima, θ_a dihedral angle of the complexed disulfide estimated from the position of the first charge transfer absorption maximum, θ_b dihedral angle of the complexed disulfide estimated from the separation between the charge transfer absorption maxima,

n not measured

f assumed value

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